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ORIGINAL CONTRIBUTION

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Adsorption kinetics at air/solution interface studied by maximum bubble pressure method

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Abstract A general dynamic surface adsorption equation $\Gamma(t)$ for maximum bubble pressure method was derived by solving Fick's diffusion equation for the bubbles under different initial and boundary conditions. Different from the planar surface adsorption(Ward-Tordai equation), the derived dynamic surface adsorption $\Gamma(t)$ for the short time consists of two terms, one of them reflects the geometric effect caused by the spherical bubble surface. This kind of effect was discussed.

The equilibrium surface tension γ_{eq} and the dynamic surface tension $\gamma(t)$ of aqueous $C_{10}E_8(CH_3(CH_2)_9(OCH_2CH_2)_8OH)$ solution at temperature 25 °C were measured by means of Wilhelmy plate method and maximal bubble pressure method respectively. In the region of $t \to 0$ (short time limits) a good agreement of experimental results with the theory was reached and the adsorption was controlled by diffusion. However, for the long time limits, a mixed diffusion-kinetics controlled process was proved.

Keywords Adsorption kinetics · Dynamic surface tension · Maximum bubble pressure method

Introduction

As a classical equation, the following Ward-Tordai equation [1] is always cited in the literature [5, 6, 7, 10] to study diffusion-controlled adsorption kinetics at air/solution interfaces:

$$\Gamma(t) = 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \frac{1}{2}\int_0^t \frac{\phi(u)}{\sqrt{t-u}}\mathrm{d}u\right] \quad \text{(general)} \qquad (1)$$

$$\Gamma(t) = 2c_0\sqrt{\frac{Dt}{\pi}} \quad \text{(for the short time limit)} \qquad (2)$$

To derive these equations, the following diffusion equation for planar surface was adopted:

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2} \qquad (3)$$

However, for the maximum bubble pressure method [2, 3, 4, 5, 6, 7, 8, 9, 10], which is one of the popular methods to be used to measure dynamic surface tensions$\gamma(t)$, the adsorption surface is no longer planar. In this paper, we will focus on this point and try to derive an equation for that case. To test the derived equations, surfactant $C_{10}E_8$ was chosen and its adsorption kinetics at air/solution was studied.

Theory

According to the principle of the maximum bubble pressure method, the gas bubbles will be created in the solution at the top of the capillary in order to measure the surface tensions of aqueous solutions. When the bubble radius equals the radius of the capillary, the pressure in the bubbles will correspond to the maximum pressure $p_{\max}$. Through measuring this maximum pressure we can calculate the surface tension γ using the Young-Laplace equation. If during the measurement the equilibrium state is slow to be established, what we have measured is then the maximum pressures at different times t ($p_{\max}(t)$) and the calculated surface tension will correspond to the dynamic surface tension $\gamma(t)$. This kind of time dependence is caused by the diffusion of the molecules of the surfactant from the bulk phase to the subsurface phase. Here the diffusion profile is not a constant (Fig. 1). The direction of the diffusion is towards the center of the bubble in which case the subsurface will correspond to $r=r_0$,r_0 being the radius of the capillary.

Here we assume that a half-spherical air/solution surface will be developed (Fig. 1). Then the diffusion equation (Fick's second law) for this case reads

$$\frac{\partial c(r,t)}{\partial t} = D\frac{\partial^2 c(r,t)}{\partial r^2} + \frac{2D}{r}\frac{\partial c(r,t)}{\partial r} \tag{4}$$

where $c(r,t)$is the concentration, at the coordinate normal to the surface r ($r \geq r_0$) and at the time t. D is the diffusion coefficient.

To solve Eq. (4) the following initial condition and boundary conditions are necessary:

$$\text{i.C.}\quad c(r,0) = c_0 \tag{5}$$

$$1^{\text{st}}\ \text{b. C.}\quad \lim_{r\to\infty} c(r,\ t) = c_0 \tag{6}$$

$$2^{\text{nd}}\ \text{b. C.}\quad c(r_0,t) = \phi(t) \tag{7}$$

where c_0 is the bulk concentration and $\phi(t)$ is the subsurface concentration.

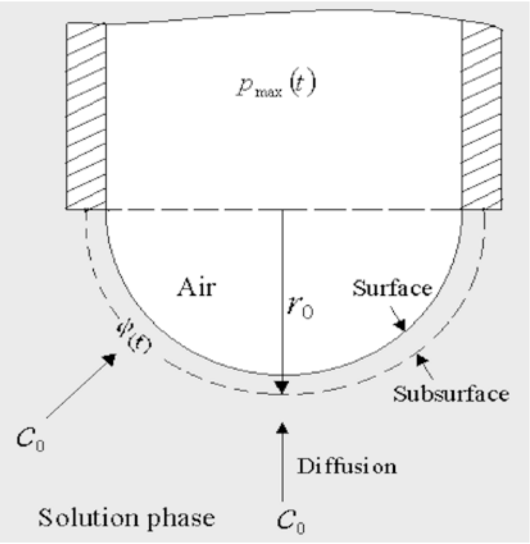

Fig. 1 Schematics of the gas bubble in solution

By means of Laplace transformation, we get the solution of Eq. (4) under the above initial and boundary conditions:

$$\begin{aligned} c(r,t) \quad &= c_0 - \tfrac{r_0}{r}[c_0 - \phi(t)] + \tfrac{2[c_0-\phi(0)]}{\sqrt{\pi}}\tfrac{r_0}{r}\int_0^{\frac{r-r_0}{2\sqrt{Dt}}} \exp\left(-z^2\right)\mathrm{d}z \\ &\quad - \tfrac{2}{\sqrt{\pi}}\tfrac{r_0}{r}\int_0^t \phi'(u)\left[\int_0^{\frac{r-r_0}{2\sqrt{D(t-u)}}} \exp\left(-z^2\right)\mathrm{d}z\right]\mathrm{d}u \quad (r \geqslant r_0) \end{aligned} \tag{8}$$

To derive the dynamic surface adsorption $\Gamma(t)$, Fick's first law at $r=r_0$ will be used:

$$\left.\frac{\mathrm{d}\Gamma(t)}{\mathrm{d}t}\right|_{r=r_0} = D\left.\frac{\partial c(r,t)}{\partial r}\right|_{r=r_0} \tag{9}$$

Inserting Eq. (8) into Eq. (9) and carrying out the integration at $r=r_0$ yields

$$\begin{aligned} \Gamma(t) &= \frac{Dc_0}{r_0}t - \frac{D}{r_0}\int_0^t \phi(t)\mathrm{d}t \\ &\quad + 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t} - \int_0^t \frac{\phi(u)}{2\sqrt{t-u}}\mathrm{d}u\right] \end{aligned} \tag{10}$$

This solution is the general diffusion-controlled equation for spherical surface adsorption (maximum bubble pressure method). The difference between Eq. (10) and the result of Ward and Tordai (Eq. 1) is the first two terms. Both of these terms are functions of the radius of the capillary r_0. They reflect the geometric effect of the spherical surface on the adsorption. For the limit case $r_0 \to \infty$, the first two terms tend towards 0 and we have the result for the planar surface, the so-called Ward-Tordai equation, correctly. Thus Ward-Tordai equation is only a limit result of our equation when $r_0 \to \infty$.

In adsorption kinetics study, two cases for the short time and long time limits will be discussed [10].

The short time limit adsorption

For the short time limit, i.e., at the early stages of diffusion, the backward movement of solute can be neglected, because the surface is sufficiently empty to take up solute molecules as soon as they arrive. Hence there is

$$\phi(t) = 0 \tag{11}$$

then Eq. (10) is reduced to

$$\Gamma(t) = \frac{Dc_0 t}{r_0} + 2c_0\sqrt{\frac{Dt}{\pi}} \tag{12}$$

Compared with the result of Ward-Tordai equation for the short time limit (Eq. 2), the dynamic adsorption for the spherical model consists of two terms. The second term is the same as Ward-Tordai equation, while the first one reflects the geometric effect on adsorption. The diffusion profile decreases with the decreasing of r and it results in the increasing of the dynamic adsorption (Fig. 1). By setting $r_0 \to \infty$, the first term is zero and the result for the planar surface, the so-called Ward-Tordai equation will be obtained, correctly.

The long time limit adsorption

The other limit case of the general equation (Eq. 10) is the long time adsorption. After a certain long time t_1, the subsurface concentration will also trend to a constant, here we assume it as c_s. Then the whole time range can be divided into two parts: $0 \to t_1$ and $t_1 \to t$. For the first time range there is

$$\Gamma_1(t_1)|_{0\to t_1} = \frac{Dc_0}{r_0}t_1 - \frac{D}{r_0}\int_0^{t_1}\phi(t)\mathrm{d}t + 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t_1} - \int_0^{t_1}\frac{\phi(u)}{2\sqrt{t_1-u}}\mathrm{d}u\right] \tag{13}$$

For the second one, we have

$$\Gamma_2(t)|_{t_1\to\, t} = (c_0 - c_s)\left[\frac{D(t-t_1)}{r_0} + 2\sqrt{\frac{D}{\pi}}\left(\sqrt{t}-\sqrt{t_1}\right)\right] \tag{14}$$

then for the whole time range

$$\Gamma(t) = \Gamma_1(t_1)|_{0\to t_1} + \Gamma_2(t)|_{t_1\to t} = (c_0 - c_s)\frac{D}{r_0}\left(t + 2r_0\sqrt{\frac{t}{D\pi}}\right) + Q \quad (t \geqslant t_1) \tag{15}$$

where $Q = \frac{Dc_0}{r_0}t_1 - \frac{D}{r_0}\int_0^{t_1}\phi(t)\mathrm{d}t + 2\sqrt{\frac{D}{\pi}}\left[c_0\sqrt{t_1} - \int_0^{t_1}\frac{\phi(u)}{2\sqrt{t_1-u}}\mathrm{d}u\right] - (c_0 - c_s)\left(\frac{Dt_1}{r_0} + 2\sqrt{\frac{Dt_1}{\pi}}\right)$,; it is only a function of t_1 and c_s.

The relationship between $\gamma(t)$ and $\Gamma(t)$

For a diffusion-controlled adsorption mechanism, an equilibrium adsorption isotherm, for example the Langmuir isotherm, can be applied as a relation between the dynamic surface tension $\gamma(t)$ and the dynamic adsorption $\Gamma(t)$ [10]:

$$\gamma(t) = \gamma_0 + RT\Gamma_\infty \ln\left[1 - \Gamma(t)/\Gamma_\infty\right] \tag{16}$$

where Γ_∞ is the saturation adsorption, γ_0 the surface tension of the solvent (water), T is the temperature, and R the ideal gas constant. Developing the logarithm in Eq. (16) into a power series and breaking off after the first term leads to the following approximation:

$$\gamma(t) = \gamma_0 - RT\Gamma(t) \tag{17}$$

Applying Eq. (12) and Eq. (15) to Eq. (17) yields for the short time limit(adsorption with no back-diffusion)

$$\gamma(t) = \gamma_0 - RT\frac{Dc_0 t}{r_0} - 2RTc_0\sqrt{\frac{Dt}{\pi}} \tag{18}$$

and for the long time limit adsorption

$$\gamma(t) = \gamma_0 - RT\left[(c_0 - c_s)\frac{D}{r_0}\left(t + 2r_0\sqrt{\frac{t}{D\pi}}\right) + Q\right] \quad (t \geqslant t_1) \tag{19}$$

Experimental

The equilibrium surface tensions were measured with a Wilhelmy plate tensiometer (K12 from the Company Krüss GmbH Hamburg, Germany). The dynamic surface tensions measurements were carried out by means of a maximum bubble pressure tensiometer (BP-2 made by Krüss GmbH Hamburg, Germany). The capillary radius was $r_0 = 0.132$ mm. $C_{10}E_8$ was purchased from SIGMA-ALDRICH Chemie, Fluka, Swiss, with a

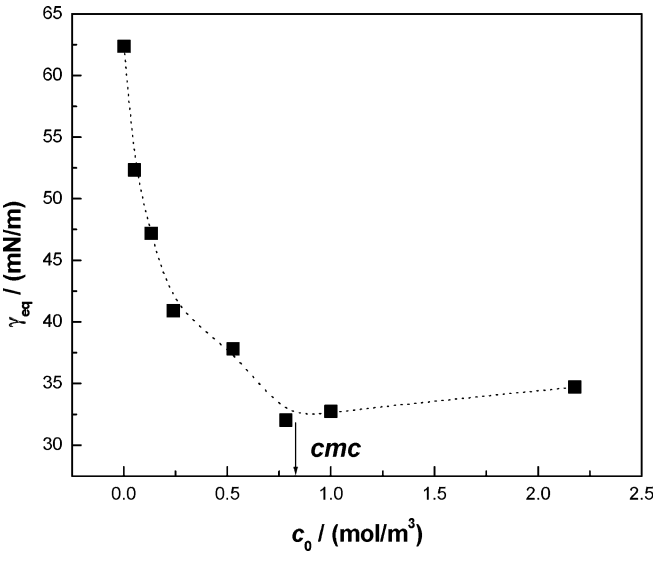

Fig. 2 Experimental equilibrium surface tensions of aqueous $C_{10}E_8$ solutions at 25 °C

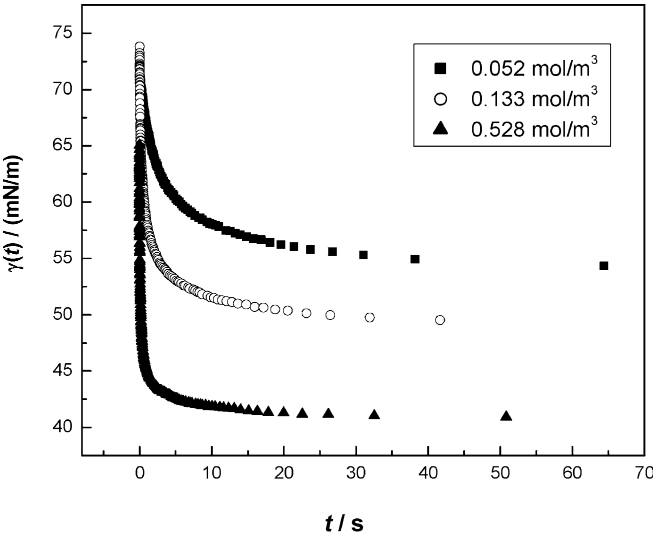

Fig. 3 Experimental dynamic surface tensions of aqueous $C_{10}E_8$ solutions at 25 °C

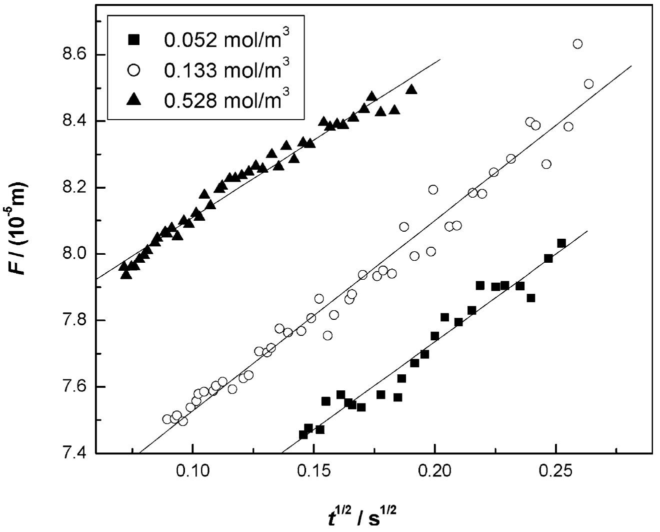

Fig. 4 The linear relation between F and $\sqrt{t}$ for the adsorption of aqueous $C_{10}E_8$ solutions at 25 °C in the short time range

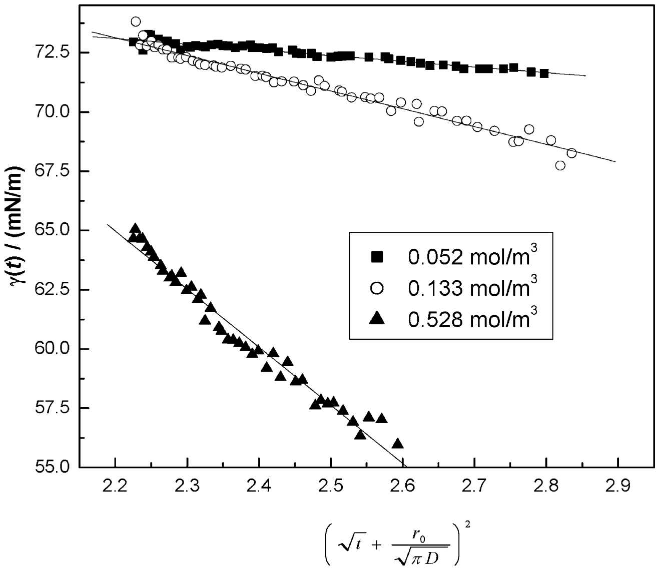

Fig. 5 The linear relation between $\gamma(t)$ and $\left(\sqrt{t}+r_0/\sqrt{\pi D}\right)^2$ for the adsorption of aqueous $C_{10}E_8$ in the short time range

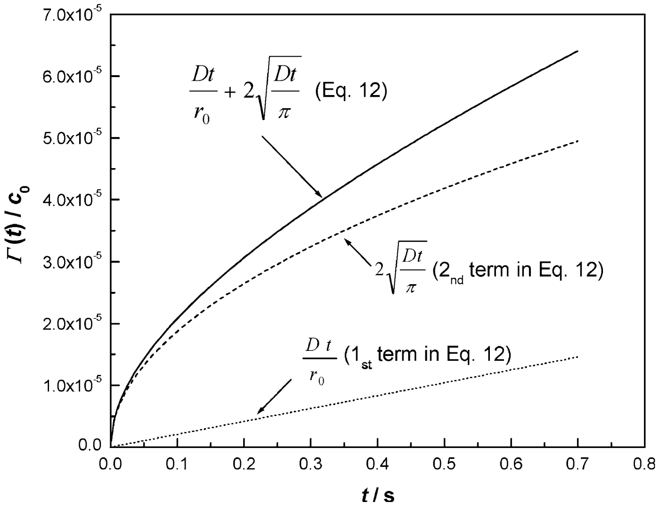

Fig. 6 The geometric effect on the adsorption (here $D = 2.75\times10^{-9}$ m^2/s was used)

purity for gas chromatography. The surfactant was used without any further purification. Three aqueous surfactant solutions, below the CMC, were prepared using double distilled and deionized water. The final distillation was performed over alkaline $KMnO_4$ so that the effect of surface active impurities was removed. All measurements of dynamic surface tension were performed at 25 ± 0.1 °C.

Results and discussions

To determine *cmc* of surfactant $C_{10}E_8$, the equilibrium surface tensions γ_{eq} of its aqueous solutions are measured and plotted in Fig. 2. The *cmc* at 25 °C is 0.83 mol/m^3. In the adsorption kinetics studies, the concentrations should be below *cmc* so that the effect of micelle on adsorption doesn't exist.

The experimental dynamic surface tensions of aqueous $C_{10}E_8$ solutions at 25 °C are shown in Fig. 3. The initial value of the surface tension equals that of pure water, which means that the solute is not adsorbed at the surface and the surface is empty at the beginning ($t \to 0$). This is the reason why $\phi(t) = 0$ for the short-time range.

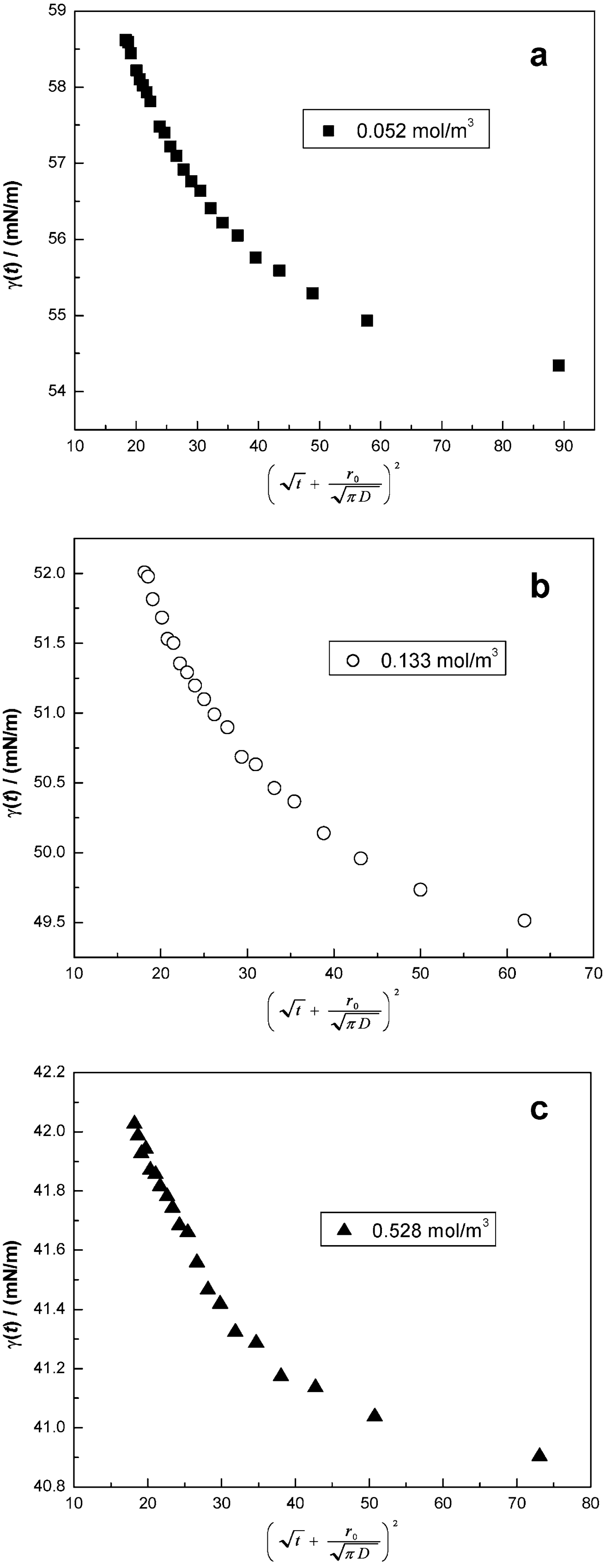

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Fig. 7a–c The relation between $\gamma(t)$ and $\left(\sqrt{t}+r_0/\sqrt{\pi D}\right)^2$ for the adsorption of aqueous $C_{10}E_8$ solutions of various concentrations at 25 °C in the long time limit ($t > 8000$ ms)

For the short time limit, we can calculate the diffusion coefficient according to Eq. (18) from the measured dynamic surface tensions $\gamma(t)$. From Eq. (18) one can see that there is no more linear relationship between $\gamma(t)$ and $\sqrt{t}$, which exists for the planar surface adsorption [10]. To overcome this difficulty and obtain diffusion coefficient D, Eq. (18) was rearranged in the following form:

$$\sqrt{\frac{r_0(\gamma_0-\gamma(t))}{RTc_0}+\frac{r_0^2}{\pi}}=\sqrt{Dt}+\frac{r_0}{\sqrt{\pi}} \tag{20}$$

where we let $F=\sqrt{\frac{r_0(\gamma_0-\gamma(t))}{RTc_0}+\frac{r_0^2}{\pi}}$, then Eq. (20) indicates that there should be linear relationship between F and $\sqrt{t}$ for a diffusion-controlled process. Figure 4 shows such kind of expected linear relationship and a pure diffusion-controlled mechanisms is proved for the short time limit. From the slope, the diffusion coefficient D was calculated. The result is 2.75×10^{-9} m^2/s.

To check the calculated coefficient, Eq. (18) can also be rearranged in the following form:

$$\gamma(t)=\gamma_0-\frac{RTD}{r_0}c_0\left(\sqrt{t}+\frac{r_0}{\sqrt{\pi D}}\right)^2+\frac{RTr_0}{\pi}c_0 \tag{21}$$

which means for short-time adsorption, the linear relation between the dynamic tension $\gamma(t)$ and $\left(\sqrt{t}+\frac{r_0}{\sqrt{\pi D}}\right)^2$ should exist. Figure 5 shows such a linear relationship. One can see that the experimental data are in good agreement with the theory.

In order to illustrate the geometric effect of this model on adsorption, two parts of Eq. (12) were plotted in Fig. 6. To plot it the calculated diffusion coefficient $D=2.75\times10^{-9}$ m^2/s for $C_{10}E_8$ was used. It shows us that for very small capillary radius and long adsorption time the geometric effect must be considered.

For the long time limit, Eq. (19) can be written in the following form:

$$\gamma(t)=\gamma_0-\frac{RTD}{r_0}(c_0-c_s)\left(\sqrt{t}+\frac{r_0}{\sqrt{\pi D}}\right)^2+\frac{RTr_0}{\pi}(c_0-c_s)-RTQ \tag{22}$$

There should also be the linear relationship between $\gamma(t)$ and $\left(\sqrt{t}+\frac{r_0}{\sqrt{\pi D}}\right)^2$ according to Eq. (22) if the adsorption is only controlled by diffusion, although we don't know the values of the constant variables c_s and t_1. From the experimental results for the three concentrations, the linear relations between $\gamma(t)$ and $\left(\sqrt{t}+\frac{r_0}{\sqrt{\pi D}}\right)^2$

were not reached for the three concentrations (see Fig. 7a–c). That means the adsorption process is not more controlled by diffusion; a mixed diffusion-kinetics controlled mechanism appeared. It is easy to understand that at the beginning the new created surface is empty and the diffusion plays a dominant role, the whole process being diffusion-controlled. However, with the increasing of adsorption time, the adsorption barrier becomes more and more important.

Summary

A general equations of diffusion-controlled adsorption for the maximum bubble pressure method were derived by means of Laplace transformation. For the short-time limit, in contrast to the well-known Ward-Tordai equation for the planar surface, the surface adsorption $\Gamma(t)$ for the bubble surface consists of two parts. One of them reflects the geometric effect and is proportional to $1/r_0$. For the very small capillary this kind of effect can not be neglected. For the short-time limit, the linear relationship between $\gamma(t)$ and $\left(\sqrt{t}+\frac{r_0}{\sqrt{\pi D}}\right)^2$ has been proved from the experimental date of aqueous $C_{10}E_8$ solutions and the adsorption is really controlled by diffusion. However, for the long time limit, a mixed diffusion-kinetics controlled mechanisms was proved.

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References

1. Ward AFH, Tordai L (1946) J Chem Phys 14:453
2. Bendure RL (1971) J Colloid Interface Sci 35:238
3. Hallowell C, Hirt DE(1994) J Colloid Interface Sci 168:281
4. Iliev TH, Dushkin CD (1992) Colloid Polym Sci 270:370
5. Joos P, Fang JP, Serrien G (1992) J Colloid Interface Sci 151:144
6. Kao RL, Edwards DA, Wasan DT, Chen E (1992) J Colloid Interface Sci 148:247
7. Lunkenheimer K, Miller R, Becht J (1982) Colloid Polym Sci 260:1145
8. Mysels K (1986) Langmuir 2:428
9. Mysels K (1989) Langmuir 5:442
10. Liu J, Messow U (2000) Colloid Polym Sci 278:124